

May 24, 1894.

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

Professor Éleuthère Élie Nicolas Mascart, who was elected a Foreign Member in 1882, signed the Obligation in the Charter Book, and was admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Researches on the Electrical Properties of Pure Substances. No. I. The Electrical Properties of Pure Sulphur." By \*RICHARD THRELFALL, M.A., Professor of Physics in the University of Sydney; JOSEPH HENRY DRAPIER BREARLEY, Deas-Thomson Scholar in the University of Sydney, and J. B. ALLEN, Exhibition Commissioners' Scholar of the University of Adelaide, South Australia. Communicated by Professor J. J. THOMSON, F.R.S. Received April 19, 1894.

(Abstract.)

Since there appears to be no definite information as to the electrical properties of pure elemental substances which are not metals, an attempt has been made to provide the necessary data in the case of sulphur. This element was chosen as being capable of easy purification, and because it can exist in a variety of forms, from the comparison of the electrical behaviour of which some information was expected to be obtained. The experimental work was begun in 1886, and some preliminary results were published by one of the authors and Mr. J. A. Pollock in the 'Philosophical Magazine' for 1890. These results referred to the construction of galvanometers for high resistance measurements, the reliability of the Clark cell as a source of small constant currents, and a method of using the galvanometer in resistance measurements in such a way that no galvanometer law of current measurement needs to be assumed.

\* Part I by Professor Threlfall and Mr. Brearley. Part II by Professor Threlfall and Mr. Allen.

This method consists in observing the galvanometer indication of a current passing through the substance of high resistance under a known voltage, and subsequently causing the galvanometer to give the same deflection, by supplying it with a known fraction of the voltage of a Clark cell, and allowing this to act on the galvanometer when the latter is in series with a wire megohm standard. The discussion of this method, depending as it does on the behaviour of Clark cells from which currents are being taken, shows that it is reliable; but it is not intended here to go over the preliminary ground covered by the papers referred to. A considerable portion of the investigation of which the paper is an account, and which extends from 1889 to the present time (October, 1893), was made conjointly with Mr. Pollock.

The first part of the paper deals with the purification of sulphur as obtained from several sources, with the result that, in the end, the following method was exclusively adopted. This method is based on the use of sulphur recovered by the Chance process, which comes into commerce as pure to at least one part in ten thousand, and results from burning hydrogen sulphide from alkali waste with insufficient air for complete combustion. The commercial product is melted, and filtered through glass wool and platinum gauze. It is then twice distilled, in such a manner as to be free from exposure to dust: and sometimes it was subsequently freed from gas, by heating in a vacuum to near the boiling point. The purity of the resulting sulphur is tested by the following criteria. It must be free from smell. It must leave no residue on evaporation from a platinum dish. When cooled suddenly from a high temperature, it must remain of a clear yellow colour: when perfectly crystalline it must be absolutely soluble in carbon bisulphide. The absence of arsenic and selenium from the sulphur employed, was proved to about one part in a million by burning the sulphur to trioxide and applying the appropriate tests. The reaction by sulphur dioxide test for selenium, when properly carried out, is more delicate than the Marsh's test for arsenic, even when the smell of the hydrogen is adopted as a criterion. If a perceptible mirror of arsenic is to be accepted as a criterion, the arsenic test is still less delicate.

A number of experiments are described, tending to show that neither arsenic nor selenium can possibly exist to any appreciable extent in alkali waste produced in the Leblanc process, so that the Chance sulphur is probably more free from these impurities than the limit we can reach by analysis. All other known impurities are got rid of by distillation and exhaustion *in vacuo*.

Section 3 of the paper deals with a discussion of various methods of measuring high resistances, and gives the detail of the method adopted by us for rapidly effecting alternate measurements of

resistance and capacity. The method of producing films of pure sulphur between aluminium electrodes is also explained. It is necessary to perform the melting, &c., in a gold vessel.

Section 4 of the paper deals with the method of constructing galvanometers of high sensitiveness and resistance. In order to observe as small currents as possible, advantage was taken of every circumstance, both of observation and construction, likely to lead to enhanced sensitiveness. For instance, instead of observing the steady deflection, we habitually observed the throw of the needle on reversal of the current through the galvanometer. The steady deflection was only observed as a check.

The highest degree of sensitiveness we ever found it necessary to use, was such that the throw on reversal was 1 micrometer division for a current of  $1.5 \times 10^{-13}$  ampères, with a period of vibration of about 25 seconds. 1 micrometer division is divisible into five parts, so that the sensitiveness for least observable throw on reversal is  $3 \times 10^{-14}$  ampères. This sensitiveness, however, cannot be taken advantage of, except with very elaborate contact keys, and under rare conditions of magnetic steadiness. We adopted the Kelvin type of instrument. We consider that the problem of sensitive galvanometer building has not hitherto been approached in the proper manner. Almost any first-rate instrument will give enormous sensitiveness on occasion: but this sensitiveness is, in general, accompanied by instability, and is useless in practice, on account of zero changes. The really important matter is to ensure the presence of high sensitiveness with ease and certainty, not after hours of adjusting, but immediately on the necessity arising; in this we have been perfectly successful. Success in this matter depends entirely on a large number of details, for a discussion of which the paper must be consulted. Exact drawings are also provided, both of the instrument as a whole, and of the more important subsidiary parts. The following notes must suffice here.

1. It is essential that the coils shall be adjustable to the magnetic system after the latter is mounted.

2. Astaticism of sufficient perfection can only be secured by the simultaneous magnetisation of all the members of the magnetic system when they occupy their final relative positions. This necessitates special appliances.

3. If copper wire is used for the coils, no other metal must be included in the circuit or connections of the instrument, otherwise thermo-electric effects cannot be avoided.

4. The instrument has four tiers of coils and magnets, whereby improved electromagnetic conditions are obtained.

5. The most important part of the instrument is that which belongs to the adjusting of the magnetic control. This must be

exceedingly stiff and well made, supported quite independently of the astatic system, and capable of the finest adjustment.

6. Stability of zero depends chiefly on the uniformity of the controlling field all over the suspended system; this is, perhaps, best obtained by using very large and symmetrically disposed magnets above and below the suspended system.

7. When this is attended to, there is no advantage in using a "tail" magnet.

8. The chief remaining difficulty is found to be due to continual small changes taking place in the direction of the earth's horizontal field. This is best overcome by attending to the astaticism of the magnets, and using a fairly strong uniform controlling field opposed to that of the earth.

9. It is essential that the instrument be entirely surrounded by massive iron screens.

10. A novel method of illumination has been worked out, ensuring uniformity of brightness of the scale images, without any appreciable heating of the galvanometer. The transparent divisions of an opaque scale are caused to give rise to interference fringes, which are then observed in a telescope with a micrometer scale in the eyepiece. Readings of the position of the magnetic system to one second of arc can be easily and certainly made.

11. The most important improvements we have made relate to the insulation of the instrument, the minute adjustment of the controlling field, the recognition of the necessary conditions for high sensitiveness combined with stability, and the method of optical magnification. The instrument can now be used at the sensitiveness mentioned with all the ease and certainty which is generally attained with a millionfold less sensitiveness.

12. Further improvements can be made by using some material of greater strength than glass for the mirror, and by improved magnetic screening. Our screens were of cast iron, and weighed about 300 pounds; the screening was not nearly sufficiently perfect.

Section 5 contains an account of a large number of experiments extending over three years on the phenomena of conduction in sulphur—of which the following are the chief results.

Crystalline sulphur, whether monoclinic or "aged" monoclinic—(which we have ventured to distinguish as a distinct variety, since it preserves the melting point, but is divested of the crystallographic properties of fresh monoclinic sulphur) has a specific resistance of  $10^{28}$  C.G.S. units as a minimum. By exposure to the air of a room the sulphur condenses moisture, which reduces its apparent specific resistance, but not nearly so much as in the parallel case of glass. The total residual charge is either absent, or less than four parts in ten thousand of the original charge, when a film of sulphur about a

quarter of a millimeter thick is charged for ten minutes with about 300 volts. By very careful drying we have succeeded in reducing the residual charge with a film of mica 0.2 mm. thick to about 1 per cent. of the original charge under similar circumstances.

In view of the want of homogeneity in the crystalline sulphur film this freedom from residual effect is noteworthy, and is perhaps to be explained by the entire absence of conductivity.

Crystalline sulphur has an electric strength which is more than enough to support 33,000 volts per centimeter—how much more we do not know. At 75° C the specific resistance with 285 volts per quarter millimeter falls to about  $6.8 \times 10^{25}$  C.G.S. The specific inductive capacity increases slightly as the temperature rises. As the temperature of the sulphur rises the conductivity increases slightly up to the melting point, when there is an enormous increase.

When a film containing about 5 per cent. of insoluble sulphur produced by cooling rapidly from a temperature above 170° C is examined, it is found to have a sensible conductivity which is not due to surface action, for it is not altered by fusing quartz rods into the exposed part of the surface, nor by blowing air saturated with water vapour against the surface. The conductivity depends on the exact composition of the mixture of soluble and insoluble sulphur, but may be taken at from  $10^{25}$  to  $10^{26}$  C.G.S. units for a film containing from three to six per cent. of amorphous unstable sulphur at ordinary temperatures. This conductivity is always greater when the voltage of about 300 volts on a film a quarter of a millimeter thick is first applied, or reversed. It is established that the increased conductivity occurs after the sulphur has rested—whether the voltage is applied for the first time, or whether it has been applied before in either direction. When the voltage is reversed this effect is more strongly marked, and the conductivity only settles to a steady value after a considerable time. The conduction, either when the current is steady, or when it commences or is reversed, does not obey Ohm's law either for small voltages (say eight volts) or large ones (say 300) when the film is 0.25 mm. thick. The deviation is, however, greater at high voltages, and greater when the "commencing" or "reversing" effects are taking place than when the conduction is steady. The deviation is always in the direction of making the conduction at high electromotive intensities greater than at low. The specific inductive capacity of a mixture of soluble and insoluble sulphur is markedly higher than that of purely crystalline sulphur. We have some evidence that the changes occurring during the first few days after the film is made lead to an increase of specific inductive capacity. The temperature coefficient of the specific inductive capacity is positive, and of the order  $2 \times 10^{-6}$  per degree between 20° and 70° C.

The residual charge is larger than when the sulphur is purely soluble, and with about 400 volts per millimeter is about 187 per cent. of the initial charge after 10 minutes' charge; the condenser being discharged for a fraction of a second and left for 10 minutes. At lower electromotive intensities it is rather greater in comparison with the initial charge, sufficiently so to be distinctly noticeable.

On heating the sulphur the conduction increases from about 50° C, in fact whenever the process of annealing takes place. When the annealing change (destruction of amorphous sulphur, and formation of soluble sulphur) is taking place rapidly the conduction is considerable. Many attempts made for the purpose of deciding whether the increase of conductivity depends on the mere proportion of insoluble sulphur present, or whether it depends on the rate at which the conversion process is taking place, yielded no absolutely certain results, but the evidence, such as it is, points to the latter as being probably the most important—but we do not consider that it can explain the conductivity at low temperatures. This conductivity is essentially discontinuous, and in this resembles the conduction through moisture films condensed on glass, ebonite, and sulphur itself.

Several of the above-mentioned peculiarities of sulphur conduction were observed by Quincke in the case of insulating liquids, and were ascribed, in part at all events, to the action of dust motes in the liquids. There is no doubt, however, that in the case of sulphur these effects are inherent to the process of conduction, for they were as strongly marked in what we consider to have been our purest film (as tested by the colour) as in the least pure one. There is some evidence that mixtures of insoluble and soluble sulphur show a maximum conductivity when the sulphur contact is between 5 and 3 per cent. All the phenomena of conduction are also noticed—the specific resistance being about the same—when we examine films containing 88 per cent. of insoluble sulphur, produced by applying enormous pressures in a testing machine to the insoluble sulphur formed on suddenly cooling sulphur from a high temperature. The sulphur, which was originally plastic, was exhausted with carbon bisulphide, and the residue treated with sulphur chloride to obtain stability. A pressure equal to the weight of 100,000 pounds on an area of say 25 square inches, causes about 12 per cent. of the insoluble sulphur to become soluble, whether it has been treated with sulphur chloride or not. Check experiments on soluble sulphur showed that the very pure benzene used to moisten the sulphur for the purpose of compression produces no subsequent change in the conductivity. The pressures were applied for from five to 10 minutes.

No change in the conductivity of mixed films was produced by stressing in alternate directions with a frequency of, say, five per second, and a voltage of from 100 to 200 volts per quarter millimeter.

A very large quantity of exact numerical data referring to these points is contained in the paper.

Part II of the paper is interposed as the facts disclosed bear on the general argument. This part of the paper bears on several correlated questions.

Section 1 deals with the contact force in air between purely soluble sulphur and mixtures of insoluble and soluble sulphur containing about 10 per cent. of the former.

The result of some rather interesting work on this point by the electrometer needle method, shows that when soluble and mixed sulphur is in contact (produced by melting the parts together), there is a contact force of the order of from one to two volts between them. The positive charge is on the insoluble sulphur. These experiments were made by using a double sulphur needle over metallic semicircles, and also by using the ordinary metallic electrometer needle over sulphur quadrants. The latter gives the best results. The phenomena are very complicated, and require to be carefully sifted; for an account of the very considerable difficulties the paper must be consulted.

Section 2 deals with the question as to whether light has any effect on the conductivity of sulphur. Monckman ('Roy. Soc. Proc.,' vol. 46, 1890) considers that he has discovered such an effect. A very large number of experiments, however, on mixed and crystalline sulphur cells, failed to indicate to us any such peculiarity, and we consider that Monckman must have been mistaken in this matter.

Section 3 deals with the qualitative phenomena of conduction in sulphur cells containing from 5 per cent. to 20 per cent. of insoluble sulphur. The general results agree with those already described, although the methods of preparing and quenching the viscous sulphur were different. The electrodes were also of platinum wire instead of aluminium plates. The temperature resistance changes are treated rather fully in this section, and bring into prominence the enormous influence of the annealing process.

Section 4 deals with a determination of the specific inductive capacity of sulphur by the method of weighing, and contains an account of the different sources of error to which we discovered the method was subject. Several ways of obtaining the required potential difference were investigated, with the result that the most satisfactory is by the use of an alternator giving a frequency of about sixty, and an induction coil used as a transformer. This avoids the difficulty which occurs when the sulphur plates get charged in virtue of their conductivity, and is noticed whenever (1) a continuously directed P.D., or (2) an unequal alternating one (as by a coil with hammer or mercury break) is used.

Part I is then continued. § 6 deals with an investigation of the specific inductive capacity of various kinds of sulphur by the method of weighing, advantage being taken of the laborious investigation of the method dealt with in Part II. Various other matters came to light, and we furnish a drawing of suitable apparatus and describe the necessary course of procedure to make the method accurate and satisfactory; in particular the proper way of preparing plates of crystalline and friable substances. The results for the specific inductive capacities are as follows, at a temperature of  $14^{\circ}\text{C}$ .

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|--|-------------|
| "Aged" monoclinic sulphur .....                            | $K = 3.162$ |
| Ditto with 1.43 per cent. insoluble unstable sulphur ..... | $K = 3.510$ |
| Ditto with 3 per cent. insoluble unstable sulphur .....    | $K = 3.75$  |

An experiment on purely amorphous sulphur is not yet ready for publication; but the above results will go a long way to clear up the great differences in the hitherto published values of this constant for sulphur. They also serve as a check on our observations on thin films, and show that our measurements of film thickness—a grave difficulty—were moderately successful.

A number of experiments bearing on a theory of conduction which we venture to suggest are also included in this part of the paper.

This is followed by an account of the theory to which our experiments led us, and which is briefly as follows. Sulphur in either of the extreme conditions does not conduct; we can only examine the purely soluble state, for the other is not sufficiently stable for a satisfactory investigation; however, we may say that changing the content of amorphous unstable sulphur from 3 per cent. to 88 per cent., produces little or no change in the conductivity. Taking this and other facts into consideration, we believe that what we have called mixtures of the two kinds of sulphur are really compounds, and that the conduction is electrolytic.

We have framed what we believe to be a novel theory of electrolysis, which explains all the facts which we have observed, and which has the peculiarity of introducing the idea of an electrolytic convection current, in connection with which the resulting changes of specific inductive capacity allow of all the phenomena of conduction observed taking place, though the charges may never really reach the electrodes. It will be seen that the effects of fatigue-reversal and the phenomena of discontinuous conduction are well accounted for by this theory. The only objections we have to it are that it is based on a molecular theory of matter, which we are persuaded requires to be remodelled, if it is to afford any real explanation of things as they are. A theory of residual effect based on the theory of conduction is



also proposed. This differs from Maxwell's theory in that the latter merely postulates changes of specific resistance and specific inductive capacity from point to point of the dielectric, while our theory is distinctly chemical. We consider that our results on mixed films are best explained by the theory we propose, though the difficulty of disproving Maxwell's theory is almost equal to the difficulty of establishing it, and we do not wish to imply that some sort of explanation on this theory may not be constructed to fit in with our observations. This is a point, however, on which we are still engaged. The matter may, perhaps, be best summed up in the statement that the evidence we have against Maxwell's theory is nearly worthless; but that we do not consider this theory necessary if our theory of conduction be accepted.

## II. "On the Dynamical Theory of Incompressible Viscous Fluids and the Determination of the Criterion." By OSBORNE REYNOLDS, F.R.S., &c. Received April 25, 1894.

(Abstract.)

The equations of motion of viscous fluid (obtained by grafting on certain terms to the abstract equations of the Eulerian form so as to adapt these equations to the case of fluids subject to stresses depending in some hypothetical manner on the rates of distortion, which equations Navier\* seems to have first introduced in 1822, and which were much studied by Cauchy† and Poisson‡) were finally shown by St. Venant§ and Sir Gabriel Stokes,|| in 1845, to involve no other assumption than that the stresses, other than that of pressure uniform in all directions, are linear functions of the rates of distortion with a co-efficient depending on the physical state of the fluid.

By obtaining a singular solution of these equations as applied to the case of pendulums in steady periodic motion Sir G. Stokes¶ was able to compare the theoretical results with the numerous experiments that had been recorded, with the result that the theoretical calculations agreed so closely with the experimental determinations as seemingly to prove the truth of the assumption involved. This was also the result of comparing the flow of water through uniform tubes with the flow calculated from a singular solution of the equations so long as the tubes were small and the velocities slow. On the other

\* 'Mém. de l'Académie,' t. vi, p. 389.

† 'Mém. des Savants Etrangers,' t. i, p. 40.

‡ 'Mém. de l'Académie,' t. x, p. 345.

§ 'B.A. Report,' 1846.

|| 'Cambridge Trans.,' 1845.

¶ 'Cambridge Trans.,' vol. ix, 1857.